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Single sensor for multiple analytes in different optical channel: Applying for multi-ion response modulation

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ABSTRACT

A Schiff-base, (2,4-di-tert-butyl-6-((2-hydroxyphenyl-imino)-methyl)phenol) (**L**), has been improved to function as a simultaneous multi-ion probe in different optical channel. The probe changes from colorless to orangish upon being deprotonated by F^-, while the presence of Al^{3+} significantly enhances the fluorescence of the probe due to the inhibition of C═N isomerization, cation-induced inhibition of excited-state intramolecular proton transfer (ESIPT), and chelation enhanced fluorescence (CHEF). Dual-channel "off-on" switching behavior resulted from the sequential input of F^- and Al^{3+}, reflecting the balance of independent reactions of Al^{3+} and F^- with **L** and with one another. This sensing phenomenon realizes transformation between multiple states and beautifully mimics a "Write-Read-Erase-Read" logic circuit with two feedback loops.

1. Introduction

Many molecular logic circuits have been developed on the basis of special recognition effects due to the importance of cation and anion detection and its potential application in information storage [1–11]. Designing sensors for multiple analytes recognition is emerging an interesting area, because of the advantages such as faster analytical processing and potential cost reductions [12–18]. Usually, multiple analytes can be detected either by sequential or simultaneous recognition. Sequential recognition of two analytes, such as one cation and one anion, usually involves an "off-on-off" [19–21] or "on-off-on" [22–24] sensing procedure taking place in one channel, which sometimes could mimic a logic circuit with memory functions. In this case, the "Write-Read-Erase-Read" logic circuits could only output signals in one channel with one feedback loop, because one kind of ions could just act one role (pen or eraser) in these system. In contrast with this, simultaneous multiple analytes recognition is more interesting, but it is difficult to operate in two channels in the same solution [16,25]. On this occasion, both kinds of ions act two roles (pen and eraser), thus signals can be read in two channels. Consequently, a dual-channel "Write-Read-Erase-Read" logic circuit with two feedback loops is potential to be constructed. This kind of logic circuits has possible implication in the development of more advanced and complex electronic devices. Therefore, our interest is to develop a reversible multiple-ion detection system with multi-state transition, and further to design functional set-reset circuits in the area of information storage [25–30].

In order to construct a system for simultaneous recognition of different analytes in two channels in the same condition, the sensor should contain different recognition sites or utilize different recognition mechanisms. Salicylidene Schiff bases are versatile ion sensors in that they form strong complexes with metal cations and undergo deprotonation and/or addition reactions with basic/nucleophilic anions [31,32]. So it is possible to realize simultaneous recognition of different analytes by using their derivatives. Of numerous common cations and anions, Al^{3+} and F^- are unusual because of their strong mutual complexation, a reaction which can therefore be brought into competition with their separate detection or sensing [33,34]. Sensors for recognition of Al^{3+} and/or F^- are numerous [33–40]. Among them, some sensors for sequential recognition of Al^{3+} and F^- have been studied [36–39]. To the best of our knowledge, a chemosensor system for Al^{3+} and F^- with dual-channel "Write-Read-Erase-Read" function has not been reported.

In our previous study, a salicylimine-based sensor **L** (Scheme S1) was used as a fluorescent sensor for Al^{3+}, then **L**-Al^{3+} ensemble was a subsequent fluorescent sensor for PPi [41]. In that case, Al^{3+} could act a pen and PPi act an eraser. The "off-on-off" sensing phenomenon caused by Al^{3+} and PPi is reversible in fluorescent channel. Herein, the reported receptor **L** has been improved to function as a simultaneous Al^{3+} and F^- probe in different optical channel. The input of only F^- or Al^{3+} produces a colorimetric or fluorescent output signal in one of the two channels, respectively. The stoichiometric addition of the counter ions leads to the reduction of the output signal, due to the formation of AlF_3, which competes with the binding between the Schiff base and

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the ions. In such a functional circuit, both of the Al^{3+} and F^- act two roles—pen and eraser, thus signals can be read in two channels. Consequently, an interesting reversible and reconfigurable multi-state "Write-Read-Erase-Read" (W-R-E-R) logic circuit possessing multi-write ability with two feedback loops is obtained.

2. Experimental

2.1. Chemicals and Instruments

3,5-di-tert-butyl-2-hydroxy-benzaldehyde was purchased from Aldrich. 2-aminophenol was purchased from Sinopharm Chemical Reagent Co.Ltd. Analytical grade solvents for synthesis and spectra were purchased from commercial suppliers. All reagents and solvents were used as received without further purification. The water used in all experiments was deionized water. Electronic absorption spectra were recorded using a Shimadzu 3100 UV–vis-NIR spectrophotometer and fluorescence spectra recorded using a Shimadzu RF-5301 PC spectrofluorimeter. Nuclear magnetic resonance spectra were recorded on a Bruker Ultra Shield 500 MHz instrument, chemical shifts being expressed in ppm using TMS as an internal standard. ESI-mass spectra were measured on Bruker Agilent1290-micrOTOF Q II. FT-IR spectra were measured on Brucker VERTEX 80 V, with samples dispersed in KBr discs. Elemental analyses were performed using an Elementar vario MICRO cube instrument.

2.2. Physical Measurements

All measurements were performed at room temperature and repeated at least once.

2.2.1. Preparation and Characterization of Reagent Solutions

A stock solution of **L** (1 mM) was prepared in DMSO. For the measurements of fluoride ion selectivity, solutions of different anions (10 mM) were prepared for F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, BF_4^-, NO_3^- as their tetrabutylammonium (TBA) salts in DMSO. Solutions containing **L** (50 μM) and each of the different anions (750 μM) were prepared by appropriate dilution and their absorption spectra were then recorded. For the measurements of Al^{3+} selectivity, solutions of different (10 mM) cations were prepared from $AlCl_3$, $BaCl_2\cdot 2H_2O$, $CaCl_2$, $CdCl_2\cdot 2.5H_2O$, $CoCl_2\cdot 6H_2O$, $CrCl_3\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$, $PbCl_2$, $FeCl_2\cdot 4H_2O$, $FeCl_3$, $HgCl_2$, KCl, $MnCl_2\cdot 4H_2O$, NaCl, $NiCl_2\cdot 6H_2O$, $ZnCl_2$ and $MgCl_2\cdot 6H_2O$ in H_2O. Solutions containing **L** (10 μM) and the different cations (100 μM) were again prepared by appropriate dilution using DMSO and their fluorescence spectra were recorded for a common excitation wavelength of 365 nm.

2.2.2. Spectrophotometric and Spectrofluorimetric Titrations

Stock solutions of **L** (1 mM) and TBAF (tetrabutyalammonium fluoride; 10 mM) were prepared in DMSO and of Al^{3+} (10 mM) by dissolving $AlCl_3$ in H_2O. Solutions containing **L** (50 μM) and increasing concentrations of F^- (0–900 μM) were prepared by appropriate dilutions and their absorption spectra (300–650 nm) recorded. Solutions containing **L** (10 μM) and increasing concentrations of Al^{3+} (0–100 μM) were prepared by appropriate dilutions using DMSO and their emission spectra (450–650 nm) recorded for an excitation wavelength of 365 nm.

2.2.3. Job Plot Measurements

For F^-, a series of solution containing **L** and F^- were prepared such that the total concentration of F^- and **L** was 100 μM. The mole fraction of F^- was varied from 0.1 to 1.0. The absorbance at 448 nm was plotted against the molar fraction of F^-. For Al^{3+}, a series of solution containing **L** and Al^{3+} were prepared such that the total concentration of Al^{3+} and **L** was 20 μM. The mole fraction of Al^{3+} was varied from 0.1 to 1.0. The fluorescence intensity at 510 nm was plotted against the molar fraction of Al^{3+}.

2.2.4. Determination of Fluorescence Quantum Yield for Al^{3+} Binding

The quantum yield was measured at room temperature referenced to quinine sulfate in sulfuric acid aqueous solution ($\Phi_{fr} = 0.546$) and calculated according to the following equation:

$$\Phi_{fs} = \Phi_{fr} \times \frac{1-10^{-ArLr}}{1-10^{-AsLs}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

where Φ_{fs} is the radiative quantum yield of the sample; Φ_{fr} is the radiative quantum yield of the standard; A_s and A_r are the absorbance of the sample and standard at the excitation wavelength, respectively; D_s and D_r are the integrated areas of the emission for sample and standard, respectively; L_s and L_r are the lengths of the absorption cells for the sample and standard test; and N_s and N_r are the indices of refraction of the sample and standard solutions (pure solvents were assumed), respectively.

2.2.5. Determination of Detection Limit for F^- and Al^{3+}

The limits of detection (DL) of **L** for F^- and Al^{3+} were determined from the following equation:

$$DL = 3\,\sigma/K$$

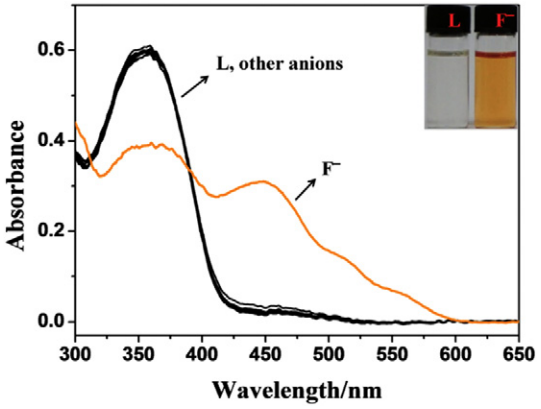

Fig. 1. Absorption spectra of **L** (50 μM) before and after addition of various anions (750 μM) of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, NO_3^- and BF_4^- in DMSO. Inset: Color change observed upon the addition of F^- to the solution of **L**.

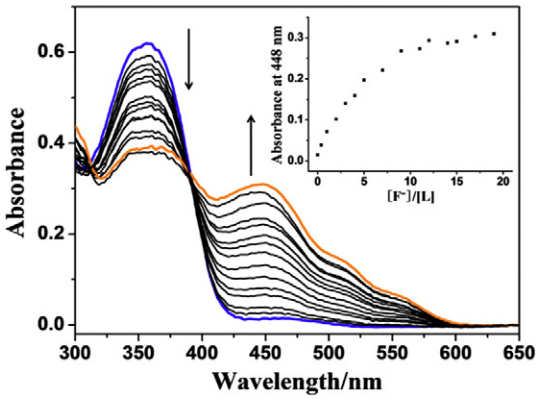

Fig. 2. Absorption spectra of **L** (50 μM) upon addition of increasing amounts of F^- (0–900 μM) in DMSO. The arrows indicate the change in the absorbance intensity with the increased F^- ions. Inset: absorbance at 448 nm versus the concentration of F^- added.